An Overview of Perchlorate Treatment (Ex Situ) Technologies

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1.0 INTRODUCTION

1.1 Overview

- Perchlorate (ClO_4^-) is the anionic component of various salts (NH_4ClO_4, $NaClO_4$, $KClO_4$)
  Results from the dissolution in water:
  e.g. $NH_4ClO_4 \Rightarrow NH_4^+ + ClO_4^-$
- ClO_4^- salts are strong oxidizers, used in a variety of industrial applications
- Generally very stable and mobile in groundwater systems
- ClO_4^- presents significant challenges in cost-effective remediation

2.0 CHARACTERISTICS OF PERCHLORATE

2.1 Reduction Pathway

OXIDIZED ClO_4^-	=>	ClO_3^-	=>	ClO_2^-	=>	ClO^-	=>	Cl_2	=>	REDUCED Cl^-
Cl(VII)		Cl(V)		Cl(III)		Cl(I)		Cl(0)		Cl(-I)
Perchlorate		Chlorate		Chlorite		Hypochlorite		Chlorine		Chloride

2.2 Mobility/Stability

- Mobility – generally very mobile:
  - Highly soluble (NH_4ClO_4: 200 mg/L)
  - Stable in many (most) subsurface environments
  - Negatively charged, little/no affinity for soil minerals (low soil-water partition coefficient value)
- Stability – generally very stable:
  - Does not readily biodegrade under most conditions and can persist for many decades.
  - Highly oxidized
  - The most stable Cl species/compounds are those in which the element is in its highest or lowest oxidation state.
  - While ClO_4^- is a powerful oxidizing agent when heated, at room temperature (characteristic of groundwater), aqueous solutions of ClO_4^- are not notable oxidizers and are extremely stable.
  - Non-volatile

EXCEPTION: Subsurface environments enriched with organic matter

2.3 Destruction

- Reduction of ClO_4^-:

  ClO_4^- => => => => Cl^- + $2O_2$

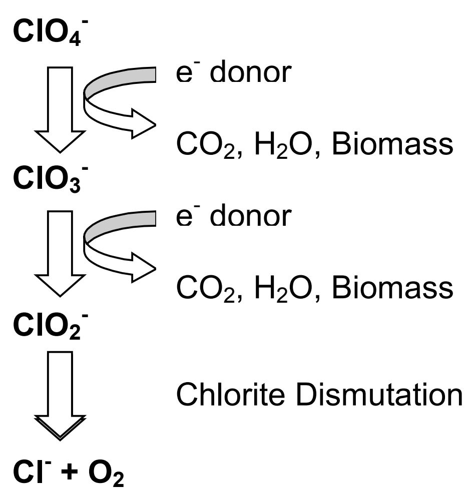
- Non-biological Reduction
  - Can be thermodynamically favored, but rate limited (chemical treatment)
  - Requires significant energy input (heat/pressure, electrical current) as well as an electron donor (substrate)
- Biological Reduction
  - ClO_4^- serves as a terminal electron acceptor in microbial respiration
  - Requires an energy source (electron donor)
  - Appropriate environmental conditions
    - ClO_4^- reduction will occur following consumption of more energy-efficient electron acceptors

Electron acceptor	Product	$Eh_{(meas)}$(mV)
O_2	H_2O	600 to 400
NO_3^-	NO_2^-	500 to 200
Mn^{4+}	Mn_2^+	400 to 200
Fe^{3+}	Fe_2^+	300 to 100
SO_4^{2-}	H_2S	0 to -150
Organic Compounds (Fermentation)	H_2, CH_4	-150 to -220

ClO_4^- reduced concurrently with or immediately following NO_3^-.

2.3 Destruction (Cont'd)

- Hypothesized pathway for the biological reduction of ClO_4^-:



3.0 REMEDIATION APPROACHES

3.1 Approaches

- Approaches
  - In situ
  - Ex situ

- Overall Approach
  - Selection of a cost-effective approach (in situ or ex situ) is **highly dependent on site-specific requirements**
  - Combination of approaches may be needed

3.2 In Situ Approaches

- For remediation without extracting groundwater
  - Bioremediation
  - Phytoremediation
  - Physical/Chemical

3.3 Ex Situ

- For extracted groundwater, either in wellhead treatment scenarios or remediation scenarios
  - Physical/Chemical Technologies
    - Ion Exchange
    - Membrane Processes
    - Electrochemical Reduction
  - Biological Technologies (Bioreactors)
    - Fluidized Bed Reactors
    - Continuous Stirred Tank Reactors
    - Suspended Bed Reactors
    - Packed Bed Reactors

4.0 SUMMARY OF EX SITU TREATMENT TECHNOLOGIES

4.1 Ex Situ Ion Exchange

Approach

- ClO_4^- (along with other anions) is sorbed on positively charged IE resin
- Many different resins have been developed/used
- Types of resins:
  - Acrylic resins, with regeneration (brine) using NaCl (5-7% strength). Spent brine requires disposal.
  - Styrenic resins (more perchlorate-specific than acrylic), regeneration not economical, resin is disposed
  - Perchlorate-specific resins, with regeneration using $FeCl_3$ + HCl, brine is disposed

4.1 Ex Situ Ion Exchange (Cont'd)

- Amount of regenerant (for acrylic) can be 0.2-10% of influent flow, for perchlorate-specific resins can be less than 0.01% of influent flow
- Regenerant (brine – for acrylic resins) must be treated or otherwise disposed
  - Calgon PNDM (not well proven)
  - Biotreatment (very difficult, long retention times required, may not be cost effective)
  - Brine line (questionable approach)
- Configurations
  - Large vessels (800 ft^3+), resin is changed out
  - Small vessels (36 ft^3 to 60 ft^3), resin is changed out, or, vessels are replaced.

4.1 Ex Situ Ion Exchange (Cont'd)

Success

- Currently the furthest along, implemented at several sites. Costs can range from $100 to over $1,000 per acre foot (highly dependent on nitrate/sulfate and other ions - competition)
- Has regulatory buy-in (DHS)
- Can be implemented for high volume low concentration scenarios (well head treatment)
- Can also be implemented for low volume high concentration scenarios

4.2 Ex Situ: Membrane Processes – Reverse Osmosis/Nanofiltration

Approach

- ClO_4^- (along with all dissolved constituents) are removed through use of semi-permeable membranes
- Dissolved constituents are collected in a concentrated rejectate
- Rejectate flow can average 5-20% of influent flow
- Rejectate must be treated or otherwise disposed, biotreatment more likely than with IE brine (no added salts)
- Depending on the water quality (TDS concentration), significant pre-treatment may be required

4.2 Ex Situ: Membrane Processes – Reverse Osmosis/Nanofiltration (Cont'd)

Success

- No data available on full scale systems
- Pilot tests have indicated ability to remove perchlorate to low levels
- Laboratory bench-scale tests indicate that rejectate is biologically treatable to ND
- Costs are expected to range from a few to several hundred dollars per acre foot
- Rejectate treatment and energy costs are primary drivers for O&M cost.

4.3 Ex Situ: Biotreatment - Bioreactors

Approach

- ClO_4^- is used as an alternate terminal electron acceptor in respiration following depletion of oxygen, and is destroyed
- ClO_4^--reducing bacteria are present as a biofilm suspended freely or on media within a vessel or vessels.
- As the contaminated influent passes through the system, bacteria are fed an organic substrate (electron donor), and couple oxidation of the substrate with reduction of ClO_4^- (as well as oxygen and nitrate, if present)
- The effluent from this system is free of perchlorate, and can be disposed of appropriately.

4.3 Ex Situ: Biotreatment – Bioreactors (Cont'd)

- Different types of bioreactors:
  - Fluidized bed reactors (FBRs)
  - Continuous stirred tank bioreactors (CSTRs)
  - Packed bed reactors (PBRs)
  - Suspended bed reactors (SBRs)
  - Hydrogen-fed bioreactors

4.3 Ex Situ: Biotreatment – Bioreactors (Cont'd)

Success

- Has been implemented at several sites. Costs can range from \$100 to over \$500 per acre foot (dependent on nitrate). Typically lower O&M than ion exchange and reverse osmosis (in non-potable water scenarios)
- Has "conditional" regulatory buy-in (DHS)
- Can be implemented for high volume low concentration scenarios (well head treatment), DHS buy-in would likely be difficult
- Can also be implemented for low volume high concentration scenarios

4.4 Summary

Technology	Advantages	Disadvantages	Relative costs
Ex-Situ Ion Exchange	• Produce potable water • Predictable performance • Applicable to wellhead treatment • Has regulatory buy-in	• ClO_4^- transferred to brine • Waste stream (brine) produced requiring further treatment (1% to 10% by volume)	• Relatively high, generally recommended for well-head treatment. $150/AF for low nitrate/sulfate site. >$500/AF for high nitrate/sulfate site
Ex-Situ Membrane Processes	• Produce potable water • Applicable to wellhead treatment • Predictable performance • Applicable over a wide concentration range • Regulatory buy-in not foreseen as a problem	• ClO_4^- transferred to rejectate • Waste stream produced requiring further ClO_4^- treatment (Rejectate, 5-10X TDS of treated groundwater); disposal • High waste stream volume relative to IE (5% to 25%))	• Relatively high, expected to be competitive with IE for well-head treatment in most cases
Ex-Situ Bioreactors	• Destroys ClO_4^- • Little/no waste stream • Applicable over a wide concentration range	• Not applicable for drinking water applications (lack of regulatory buy-in)	• Relatively low, generally recommended for cases where hydraulic control is required, effluent can be spread or re-injected. <$100/AF for above low nitrate site. <$400/AF for above high nitrate site

5.0 CONCLUSIONS

Conclusions

- ClO_4^- presents significant challenges to cost-effective remediation (soluble, mobile, stable)
- Selection of cost-effective approach highly dependent on site-specific requirements
- Ex situ biological treatment show promise, most cost-effective (non-drinking water applications)
- Ion exchange appears to be method of choice for ex situ (particularly for drinking water applications)
- Membrane processes may be most cost-effective for some sites